

# Phototransformation of Dichlorophen in Aqueous Phase

Elka Mansfield & Claire Richard\*

Laboratoire de Photochimie Moléculaire et Macromoléculaire, URA CNRS n° 433, Université Blaise Pascal, 63177 Aubière Cedex, France

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**Abstract:** The photolysis of dichlorophen (DCP) in acidic medium yields 4-chloro-4'-hydroxy-2,2'-methylenediphenol (I) in the absence of oxygen and a benzoquinone-like derivative (II) in oxygenated solution. At pH = 9, DCP is in monoanionic form, and three products, I, II and 4-chloro-2,2'-methylenediphenol (III) are detected after irradiation of deoxygenated solutions of DCP. Formation of III is also observed in acidic or neutral solutions containing a low percentage of isopropanol. These results can be explained by the formation of a carbene after HCl elimination and reaction of this intermediate with water, oxygen, alcohol, anionic form of I or DCP.

**Key words:** dichlorophen, phototransformation, aqueous phase

## 1 INTRODUCTION

Dichlorophen (4,4'-dichloro-2,2'-methylenediphenol; DCP; Fig. 1) is an algicide, fungicide and bactericide with contact action. It has an acute oral LD<sub>50</sub> of 1250 mg kg<sup>-1</sup> for guinea pigs and is particularly toxic to fish.<sup>1</sup> This compound absorbs sunlight especially in the anionic forms and its direct phototransformation is a possible degradation pathway in natural waters. Therefore, it is of interest to know what the fate of DCP is when irradiated in aqueous solution.

DCP belongs to the family of 4-halogenophenols which exhibit interesting behaviour when irradiated in water. By means of nano-second laser photolysis and transient absorption spectroscopy, Grabner *et al.* showed the formation of a carbene, 4-oxocyclohexa-2,5-dienylidene in the photolysis of 4-chlorophenol.<sup>2</sup> Reaction of this intermediate with water, oxygen or 4-chlorophenol itself results in the formation of hydroquinone, *para*-benzoquinone or coupling products.<sup>3–5</sup>

## 2 EXPERIMENTAL

DCP was purchased from Merck and recrystallised from toluene before use. Water was purified with a Millipore Milli-Q device.

\* To whom correspondence should be addressed.

Monochromatic irradiations at 280 and 300 nm were carried out using a Schoeffel monochromator equipped with a 1600-W xenon lamp. Ferrioxalate was used as chemical actinometer. Photon flows were evaluated as  $6.2 \times 10^{13}$  photons cm<sup>-2</sup> s<sup>-1</sup> at 280 nm and  $1.2 \times 10^{14}$

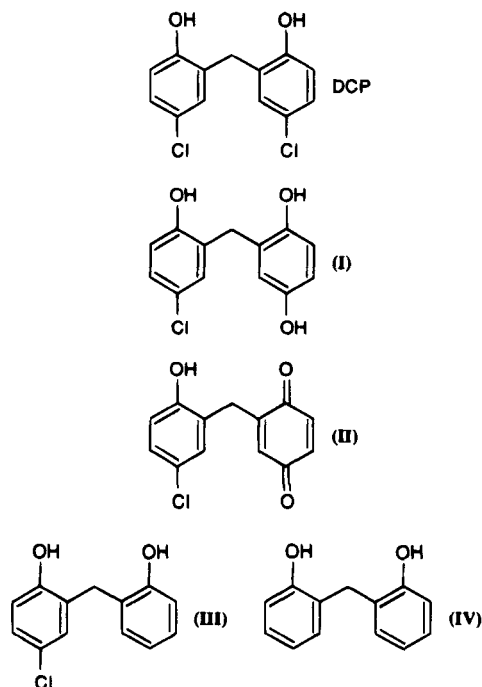


Fig. 1. Structures of compounds discussed.

photons  $\text{cm}^{-2} \text{s}^{-1}$  at 300 nm. For preparative purposes, solutions were irradiated with polychromatic light using a device equipped with a fluorescent lamp with a maximum emission located at 310 nm.

Absorption spectra were recorded on a Cary 13 Varian spectrophotometer. HPLC analyses were performed on a Merck chromatograph equipped with a photodiode array detector and a fluorescence detector in series. The column was a Merck reverse-phase  $\text{C}_{18}$ , 5  $\mu\text{m}$  (125 mm  $\times$  4 mm). Preparative HPLC was carried out on a Gilson apparatus equipped with a Microsorb  $\text{C}_{18}$  column, 3  $\mu\text{m}$  (250 mm  $\times$  20 mm).

For the determination of chloride ion concentration, the method employed involved reaction of chloride with mercury (II) thiocyanate to form a chloromercurate (II) complex ion, with release of  $\text{SCN}^-$  which formed with  $\text{Fe}^{3+}$  a red colour complex ( $\lambda_{\text{max}} = 460 \text{ nm}$ ).<sup>6</sup>

Mass spectra were obtained from 'Service de Spectrométrie de Masse', Université d'Orléans, France. [ $^1\text{H}$ ]NMR spectra were recorded on a Bruker AC 400 MHz Fourier transform spectrometer, using solutions in deuteromethanol.

### 3 RESULTS AND DISCUSSION

The two  $\text{pK}_a$  values of DCP were 7.5 and 11.5. The first  $\text{pK}_a$  value was very low compared to that of 4-chlorophenol ( $\text{pK}_a = 10$ ), probably as a result of intramolecular hydrogen bonding between the two OH groups. The molecular form of DCP had  $\lambda_{\text{max}}$  at 281 nm with an extinction coefficient of  $3800 \text{ M}^{-1} \text{cm}^{-1}$  and the monoanionic form  $\lambda_{\text{max}}$  at 301 nm with an extinction coefficient of  $5050 \text{ M}^{-1} \text{cm}^{-1}$  (Fig. 2). The solubility of the molecular form of DCP was about  $9 \times 10^{-5} \text{ M}$ .

#### 3.1 Irradiations

Slightly acidic solutions ( $\text{pH} = 5.6$ ) of DCP ( $5 \times 10^{-5} \text{ M}$ ) were irradiated at 280 nm. In a deoxygenated medium, one major photoproduct (Fig. 1) (I) was observed, whereas in oxygen-saturated solutions another product (Fig. 1; II) was formed. In both cases, the pH of the solution decreased during irradiation. UV spectra of photoproducts I and II are shown in Fig. 3. I

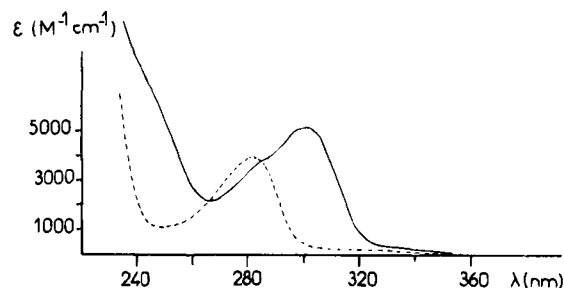


Fig. 2. UV spectrum of DCP at (---) pH 5 and (—) pH 9.

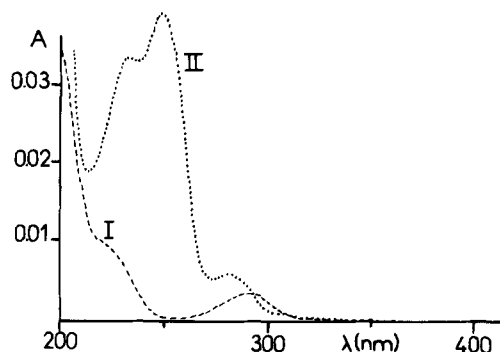


Fig. 3. UV spectra of photoproducts (---) I and (····) II.

is fluorescent with a maximum emission at 325 nm; II is not fluorescent.

Solutions of DCP ( $8 \times 10^{-5} \text{ M}$ ) buffered at  $\text{pH} = 9$  with borates were irradiated at 300 nm. In the absence of oxygen three photoproducts were detected: I, II, III (Fig. 4). In oxygen-saturated medium, II was the only product observed.

In acidic solutions ( $\text{pH} = 4$ ), neutral or basic solutions ( $\text{pH} = 9$ ) containing 2% of isopropanol, III was formed as primary product and IV as secondary product.

Many attempts were made to measure quantitatively by HPLC the decrease of DCP concentration in irradiated samples. We were unsuccessful because of a lack of reproducibility in HPLC quantitative measurements, most likely due to the low solubility of DCP. A colorimetric method was employed to determine the quantum yield of  $\text{Cl}^-$  formation, which was evaluated as 0.50 and 0.34 for the molecular form and the monoanionic form of DCP respectively.

#### 3.2 Identification of photoproducts

Photoproduct I was obtained in deoxygenated conditions, whereas, at pH higher than 6, I was oxidized by oxygen during the sampling giving II as one of the products of conversion. Acidification of the starting solution to  $\text{pH} < 5.5$  prevented the transformation of I. However, at low pH values the solubility of DCP was reduced and the concentration of photoproduct I

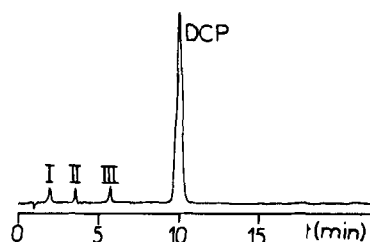


Fig. 4. HPLC chromatogram of a deoxygenated solution of DCP buffered at  $\text{pH} = 9$  and irradiated at 300 nm. Mobile phase water + methanol (50 + 50 by volume), detection set at 250 nm.

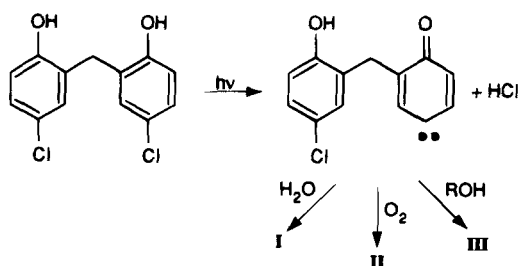


Fig. 5. Proposed reaction mechanisms.

became too low to effect its isolation by preparative HPLC.

Since it was difficult to separate photoproduct I, attempts were made to isolate product II. In order to accumulate enough II for identification, DCP was irradiated in acetonitrile + water (50 + 50 by volume), which allowed the use of much more concentrated solutions, although III was formed in addition. A  $2.5 \times 10^{-3}$  M oxygenated solution of DCP (50 ml) was irradiated in polychromatic light for 10 min and evaporated to 10 ml. Photoproduct II was separated by preparative HPLC using a methanol + water (50 + 50 by volume) as mobile phase. During evaporation of the fractions, II was reduced to I. Further deliberate heating of the sample in the presence of methanol enabled us to

observe almost complete conversion of II into I. For I, the following data were obtained: mass spectrum  $m/e$  150 and 152;  $[^1\text{H}]$ NMR  $\delta$  7.18 (d, 1H,  $J = 2.7$  Hz), 7.09 (dd, 1H,  $J = 8.3$  Hz and  $2.7$  Hz), 6.84 (d, 1H,  $J = 8.3$  Hz), 6.79 (d, 1H,  $J = 8.3$  Hz), 6.79 (d, 1H,  $J = 2.8$  Hz), 6.66 (dd, 1H,  $J = 8.3$  Hz and  $2.8$  Hz), 3.95 (s, 2H). In accordance with these results, I was confirmed to be 4-chloro-4'-hydroxy-2,2'-methylenediphenol (Fig. 1).

In neutral aerated medium, I was converted into II. As a result of the likely similarity in  $\text{pK}_a$  of I and DCP, at  $\text{pH} = 6.5$ , about 10% of I was estimated to be in monoanionic form. The anionic form of hydroquinone was known to be spontaneously oxidised by oxygen into benzoquinone. Similarly, the ionic form of I was expected to be oxidised to 2-(5-chloro-2-hydroxyphenylmethyl)-*p*-benzoquinone (Fig. 1, II). The spectrum of II presented a strong band centred at 250 nm which was characteristic of a benzoquinone-like structure. The reduction of II into I upon heating in methanolic solutions showed that II was a strong oxidant and confirmed the structure proposed for II.

The yields of conversion of DCP into I and II could not be measured accurately because of the poor reproducibility of HPLC quantitative measurements. In acidic deoxygenated solutions, the yield of I was at least

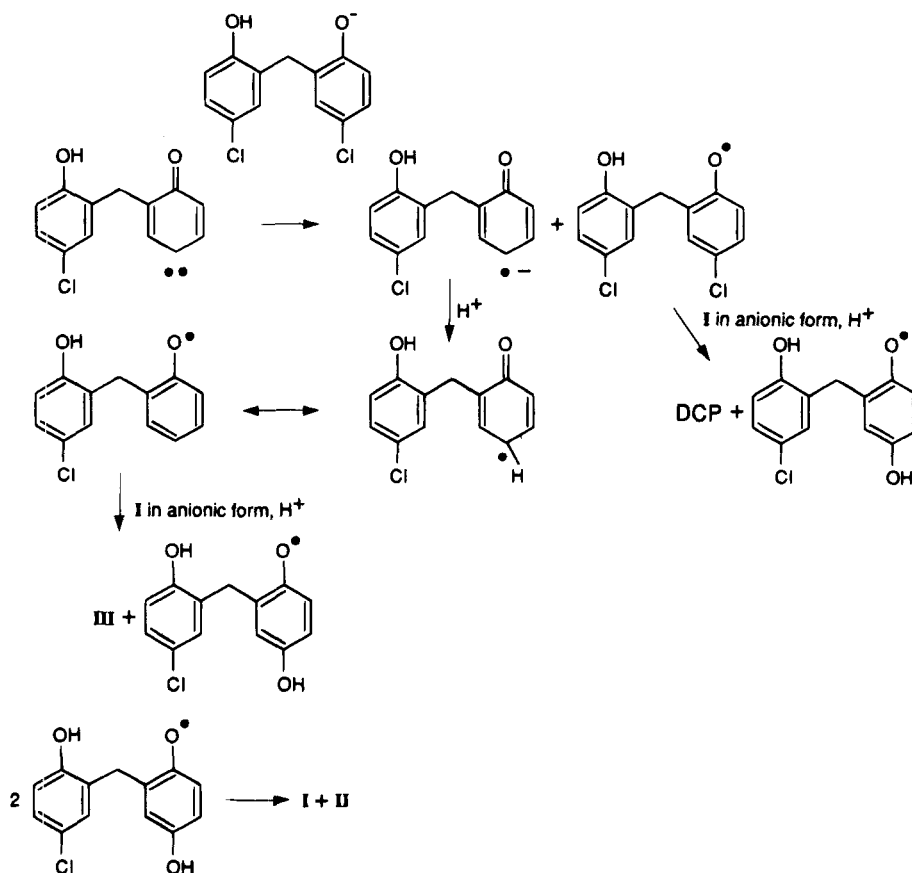


Fig. 6. Proposed reaction mechanisms in basic conditions.

70% and in acidic oxygenated medium that of **II** at least 80%.

Photoproducts **III** and **IV** were isolated from irradiated solutions of DCP containing 10% of isopropanol. For **III**, the mass spectra gave  $m/e = 234$  and  $236$  and for **IV**  $m/e = 200$ .  $^1\text{H}$ [NMR]s of **III**:  $\delta$  7.14 (d, 1H,  $J = 2.4$  Hz), 7.12 (td, 1H,  $J = 7.8$  Hz and  $1.7$  Hz), 7.04 (d, 1H,  $J = 7.8$  Hz) and (dd, 1H,  $J = 7.8$  Hz and  $2.4$  Hz), 6.87 (d, 1H,  $J = 7.8$  Hz), 6.83 (td, 1H,  $J = 7.8$  Hz and  $J = 1.7$  Hz), 6.80 (dd, 1H,  $J = 7.8$  Hz and  $1.7$  Hz), 3.95 (s, 2H). It was deduced that **III** and **IV** were the reduction products 4-chloro-2,2'-methylenediphenol and 2,2'-methylenediphenol, respectively (Fig. 1).

### 3.3 Possible mechanism of formation of products

The mechanism of the photolysis of 4-chlorophenol in aqueous medium was recently clarified.<sup>2</sup> It was shown that, after the elimination of HCl, the carbene 4-oxocyclohexa-2,5-dienylidene is produced. The formation of hydroquinone in deoxygenated solutions, *para*-benzoquinone in oxygenated medium and phenol in the presence of alcohols was explained by the reaction of this carbene with water, oxygen and H-donor molecules respectively. The results obtained with DCP are in good agreement with those obtained in the photolysis of 4-chlorophenol: formation of a hydroquinone-like derivative in deoxygenated medium, of a benzoquinone-like derivative in oxygen-saturated solutions and of reduction products in the presence of alcohols. Furthermore,  $\text{Cl}^-$  and  $\text{H}^+$  ions are released during the photolysis. Thus the mechanism shown in Fig. 5 can be proposed.

In basic medium, **II** and **III** were produced along with **I**, even in oxygen-free and alcohol-free solutions. The presence of **II** on the HPLC chromatograms of basic solutions of DCP irradiated in the absence of oxygen can be due to the thermal oxidation of the anionic form of **I** upon contact with air, after irradiation. The formation of **III** can be explained by the scheme shown in Fig. 6 in which the carbene is reduced by the anionic form of DCP and the two phenoxy radicals formed reduced by **I** into **III** and DCP. The dismutation of the two semiquinone radicals should lead to the formation of **I** and **II**. An alternative pathway for

the formation of **II** and **III** is the reduction of the carbene by the anionic form of **I** in the first step.

## 4 CONCLUSIONS

The phototransformation of dichlorophen in aqueous solution was studied as a function of several parameters: pH of the solution, absence and presence of both oxygen and isopropanol. The photolysis of acidic solutions of DCP gave rise to a hydroquinone-like product in deoxygenated conditions and to a benzoquinone-like derivative in oxygen-saturated solutions. The quantum yield was 0.50. Upon irradiation of DCP in mono-anionic form an additional reduction product was produced and the quantum yield of DCP photolysis was 0.34.

Due to the low value of its first  $\text{pK}_a$  (7.5), DCP is partly ionised in natural water and absorbs solar light. The results reported here show that in these conditions the photodegradation of DCP is an efficient process leading to compounds that are less chlorinated than the starting material.

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